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(54) Title: PLASTICIZED POLY VINYL CHLORIDE COMPOSITIONS

(57) **Abstract:** The invention relates to plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

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(54) Title: PLASTICIZED POLY VINYL CHLORIDE COMPOSITIONS

(57) Abstract: The invention relates to plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

Title: "Plasticized poly vinyl chloride composition"**Field of the Invention**

The invention relates to plasticized poly vinyl chloride compositions comprising at least one poly vinyl chloride resin and a special plasticizer compounded with said at least one poly vinyl chloride resin.

Description of the Related Art

WO 01/98404 discloses a plasticized vinyl chloride composition comprising (a) at least one vinyl chloride resin and (b) a plasticizer compounded with (a) wherein said plasticizer comprises a fatty acid product derived from a vegetable oil having at least 80% by weight of unsaturated fatty acids, wherein said fatty acids are substantially fully esterified with a monool or a polyol, and said esterified unsaturated fatty acids have been substantially fully epoxidized.

In an article entitled "Use of esterified rapeseed oil as plasticizer" in plastics processing" by Johannes Wehlmann it is mentioned that in most cases phthalic acid esters, especially dioctyl phthalate (DOP), are used as plasticizers for poly vinyl chloride (PVC) resins (see **Fett/Lipid 101, 1999, No. 6, pages 249-256**). However, phthalate plasticizers are criticized because of their environmentally harmful action. The author then describes the use of rape methyl ester as plasticizer.

Detailed Description of the Invention

It was an object of the present invention to provide plasticizers for plastics, especially PVC, which overcome the difficulties and disadvantages of the plasticizers of the prior art. It was a further object of the invention that PVC plastisol formulations based on these plasticizers show a reduced viscosity compared with formulations based on phthalic ester type plasticizers like dioctyl phthalate (DOP). As it is known to the artisan plastisols are dispersions of plastics, especially PVC, in plasticizers.

According to the invention this is achieved by **plasticized poly vinyl chloride compositions** comprising (a) 100 parts by weight of at least

one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 14 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically 5 unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

In a preferred embodiment of the invention the plasticized poly 10 vinyl chloride compositions are free of phthalic ester type plasticizers and especially free of diethylphthalate (DOP).

In another embodiment of the invention the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45.

15 The invention also relates to **plasticizer compositions** for poly vinyl chloride resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 20 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched. Preferably these plasticizer compositions are free of diethylphthalate. In one embodiment these plasticizer compositions contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. In another preferred embodiment 25 these plasticizer compositions contain exclusively compounds (i) and (ii).

The invention also relates to the **use** of compositions comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the 30 proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the pro-

viso that these fatty acids can be saturated or olefinically unsaturated, linear or branched as **plasticizers for poly vinyl chloride resins**. As stated above the compositions are preferably free of are free of phthalic ester type plasticizers.

5 As also stated above the compositions preferably contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. Those compositions which exclusively contain compounds (i) and (ii) are preferred for the use as plasticizers for poly vinyl chloride resins.

10 **Examples**

IES = Isobutyl epoxy stearate

15 **IFAME** = Mixture of methyl esters of fatty acids. The distribution of the fatty acid individuals in these methyl esters was (% means mole-%): Straight chain C12 = 0.3%, branched chain C14 = 0.4%, straight chain C14 = 1.0%, branched chain C16 = 3.7% , straight chain C16 = 4.9%, branched chain C18 = 61.4%, straight chain C18 = 4.6%, cyclic C18 = 17.5%, straight chain C20 = 0.1%, aromatic C18 = 6.1%.

Filler = Calcium Carbonate (Calcit)

20 **Stabilizer** = Stabiol CZ 3083 (Liquid Ca/Zn Stabilizer commercially available from COGNIS)

PVC = Poly vinyl chloride produced by emulsion polymerization (Solvic 374 MB commercially available from SOLVAY)

Example 1

(PVC Ball formulation)

25 The following compounds were mixed together in a conventional mixer:

PVC 100 phr

IES 60 phr

IFAME 40 phr

30 Filler 90 phr

Stabilizer 1 phr

The abbreviation phr means "parts per hundred resin" and is

known to the man skilled in the art.

The viscosity of the formulation was measured according to Brookfield (Spindle 5 at 20 rpm). It was 36.000 cps. The value of the viscosity is much lower compared to the formulation of comparative example 1 which is 5 based on dioctyl phthalate as plasticizer.

The formulation was then transferred into a ball by rotational moulding at 180 °C. The shore A hardness of the ball was measured. It was 54,8. The value of the shore A hardness is nearly the same as the shore A hardness of the ball in comparative example 1. This shows that the 10 IES/IFAME mixture is as good as plasticizer as the "classical" dioctylphthalate.

Comparative Example 1

(PVC Ball formulation)

The following compounds were mixed together in a conventional 15 mixer:

PVC	100 phr
dioctyl phthalate	100 phr
Filler	90 phr
Stabilizer	1 phr

20 The viscosity of the formulation was measured according to Brookfield (Spindle 7, 5 rpm). It was 125.400 cps

The formulation was then transferred into a ball by rotational moulding at 180 °C. The shore A hardness of the ball was measured; it was 54,0.

Claims

1. Plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.
5
- 10 2. Compositions according to claim 1 wherein said plasticized poly vinyl chloride compositions are free of phthalic ester type plasticizers.
3. Composition according to claim 1 wherein the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.
- 15 4. Plasticizer compositions for poly vinyl chloride resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.
20
5. Compositions according to claim 4 with the proviso that the compositions are free of phthalic ester type plasticizers.
6. Compositions according to claim 4 with the proviso that the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.
- 25 7. Compositions according to claim 4 with the further proviso that the compositions contain exclusively compounds (i) and (ii).
8. The use of compositions comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain
30 at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched as plastici-

zers for poly vinyl chloride resins.

9. The use according to claim 8 with the proviso that the compositions are free of phthalic ester type plasticizers.

10. The use according to claim 8 with the proviso that the weight 5 ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

11. The use according to claim 8 with the further proviso that the compositions contain exclusively compounds (i) and (ii).

INTERNATIONAL SEARCH REPORT

International application No

/BR 02/00175

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08K5/04 C08L27/06 // (C08K5/04, 5:1515, 5:101)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 934 689 A (SWIFT & CO) 21 August 1963 (1963-08-21) claims 1,8 examples IV-VI	1-11
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A	EP 0 337 237 A (NEYNABER CHEMIE GMBH) 18 October 1989 (1989-10-18) claims 1,2	1-11
A	DE 38 39 418 A (CIBA GEIGY AG) 8 June 1989 (1989-06-08) claims 1,11,13	1-11
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
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- *P* document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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